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Photo: Sophie C Casetou

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Den inter- och intraspecifika variationen för egenskaperna hos träkol i boreala ekosystem

Sophie- Charlotte Casetou

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This report presents an MSc/BSc thesis at the Department of Forest Ecology and Management, Faculty of Forest Sciences, SLU. The work has been supervised and reviewed by the supervisor, and been approved by the examiner. However, the author is the sole responsible for the content.

Abstract

Wildfire-produced charcoal has been shown to influence key soil ecological processes. However, few studies have considered the role of interacting variables in describing the wide variability of charcoal ecological traits under natural and semi-natural conditions. Our study tested how different chemical and structural properties of charcoal are affected by single and interaction effects of 1) the original wood species, 2) fire temperature, and 3) flame exposure time. We produced charcoal from three common boreal tree species (*Pinus*, *Betula* and *Sorbus*) at three different temperatures 450°C, 700°C and 900°C. The wood was exposed to 45 min at 450°C, 10 and 15 min at 700°C, and 5, 10 and 15 min at 900°C. Further, at low temperature (450°C), we compared our newly developed charring method (isolated gas flame in a barrel) with a more conventional charring procedure (muffle furnace). We also collected charcoal produced at a prescribed fire in central Västerbotten, Sweden, in order to compare natural fire conditions with our controlled high temperature charring method. Our results show that key ecological traits, such as electric conductivity (EC), transversal porosity and bulk density are dependent on temperature, species and, importantly, their corresponding interaction. Chemical charcoal properties, such as pH, NO_3^- and NH_4^+ were temperature-dependent, while pH was also influenced by the flame exposure time. Structural charcoal traits, such as pore size distribution, were strongly dependent on the original wood species, but were largely unaffected by the fire conditions. We did not detect any significant differences in charcoal properties between our barrel method and to the muffle furnace method, indicating that the barrel method successfully isolates the wood from outside oxygen during the charring process. The collected wildfire-produced charcoal showed lower pH and EC values, but higher PO_4^{3-} concentration than barrel-produced charcoal. The results from this experiment suggested that the most determining temperature in wildfire is not solely the peak temperature. The longer residence time at the lower temperatures is also a large contributing factor to the observed variation in charcoal traits. These findings of interaction effects open up the possibility to fully explain the trait variability in wood produced charcoal.

Keywords: Charcoal traits, *Sorbus aucuparia*, *Betula pendula*, *Pinus sylvestris*, Fire conditions, Interaction effects.

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1. Introduction

Wildfire is a major disturbance in boreal forest ecosystems. In northern Sweden it has a natural return interval of approximately 50-100 years (Zackrisson 1977). The charcoal layer deposited after fire is widely distributed and so represents an important constituent of boreal forest soils. Charcoal carbon contributes significantly to long-term carbon storage, especially given its slow turnover (e.g., Anderson, 1991). Mean residence times of charcoal range from centuries to millennia (Goldberg, 1985), mainly due to condensed aromatic ring structures (Preston and Schmidt, 2006) and low amount of oxygen-containing functional groups, which make it more stable than humic substances (Laird et al., 2007). Ohlson et al. (2009) extrapolated their charcoal findings for Scandinavian boreal forests to boreal forests worldwide. Accordingly, it is estimated that 1Pg of carbon is stored in the form of charcoal in boreal forest soils, which corresponds to 1 % of the total amount of carbon incorporated in boreal forest plants. Moreover wildfire is the maintaining factor for early successional forest, dominated by deciduous tree species and *Pinus sylvestris* (Zackrisson, 1977). Today these forests types are restricted to nutrient poor and dry sites. Effective wildfire suppression since the 19th century, lead to even-aged coniferous forests, dominated by the late successional species *Picea abies* (L.) Karst and the understorey species *Empetrum hermaphroditum* Hagerup and *Vaccinium myrtillus* (Zackrisson, 1977). Typical characteristics of these forest types are high amounts of allelochemical substances which inhibit nutrient mineralization and cause the development of thick acidic mor humus layer. Wildfire derived charcoal plays an essential role in rejuvenating these ecosystems (Wardle et al., 1998).

In addition to being a carbon sink (Preston and Schmidt, 2006), wildfire-derived charcoal interacts with other ecosystem components, potentially releasing carbon dioxide into the atmosphere (carbon source) and/or reducing greenhouse gas emissions of nitrous oxide and methane (Rondon et al., 2005). Amounts of 984 to 2074 kg/ha have been found to influence ecosystem processes relevant to the carbon cycle in boreal forests (Zackrisson et al., 1996). For example, Wardle et al. (2008) found that charcoal could accelerate forest humus loss in a short time period, due to enhanced decomposition of soil organic matter. At the same time, it has also been shown that charcoal stimulates sustainable plant growth, possibly increasing net primary productivity (Wardle et al., 1998; Lehmann et al., 2003). Charcoal has shown to mediate nutrient availability (Glaser et al., 2002), thereby altering soil microbial composition and abundance. Notably symbiotic associations between plants and fungi may benefit from charcoal physical and chemical properties (Warnock et al., 2007, Lehmann et al., 2011; Makoto et al. 2010). Charcoal may also directly affect plant growth by altering soil depth, texture, structure and pore space in the root zone. Such changes of soil physical properties will largely determine the availability of air and water (Kammann et al., 2011, Lehmann et al., 2011).

One mechanism by which charcoal affects ecosystem processes is adsorption of dissolved organic matter and sorption of allelochemical compounds. Previous studies have generated some understanding of how charcoal adsorbs phenol compounds from ericaceous species (Keech et al., 2005), which in turn can result in increased nitrification rates (Berglund et al., 2004; Gundale et al., 2007). The adsorptive ability is strongly related to charcoal physical

traits, such as its highly porous nature and its large surface area (Zackrisson et al., 1996; De Luca et al., 2002; Berglund et al., 2004; Hille and den Ouden, 2005; Keech et al., 2005; De Luca and Gundale, 2006). Charcoal may also increase the soil volume and reduce the soil bulk density due to its lower density compared to mineral soil (Verheijen et al., 2010; Major et al., 2010; Lehmann et al., 2011). Thus, increased aeration may reduce anaerobic soil conditions and therefore influence decomposition rates, nitrogen turnover and greenhouse gas emissions (Van Zwieten et al., 2009). Furthermore, specific surface areas of charcoal and clay are similar and may lead to a net gain in total soil surface area, especially in sandy soils (e.g. Spodosols in boreal Sweden) (Tyron, 1948; Brady and Weil, 2008; Downie et al., 2009). Soil organic matter stabilization and improved water holding capacities may result from improved soil aggregation. Charcoal was found to form organo-mineral complexes analogue to clay minerals (Piccolo et al., 1996; Krull et al., 2003; Brodowski et al., 2006). Provision of refuges from microbial grazers may be beneficial for microbial organisms, such as mycorrhizal fungi or heterotrophic and nitrifying bacteria (Ishii et al., 1994; Pietikäinen et al., 2000; Wardle, 2003; Makoto et al., 2010). Macro-pore size distribution can serve as an indicator for the soil microbial community composition, assuming that microbes differ in size and may have limited access to the internal charcoal structure. Furthermore, plant root movement as well as water holding capacities (e.g. plant available water is held in pores between 10-80 μm in charcoal), are thought to be a function of macro-pore size distribution (Lehmann et al., 2011; Keech et al., 2005; Pietikäinen et al., 2000). Charcoal may also increase soil nutrient availability by altering soil chemical properties such as pH and cation exchange capacity (CEC) (Glaser et al., 2002; Topoliantz et al., 2005a; Liang et al., 2006). Charcoal itself can readily provide nutrients for plant uptake, such as NH_4^+ , NO_3^- , and PO_4^{3-} which are present in the ash of charcoal as soluble compounds (Glaser et al., 2002). However charcoal may also be a long term source of nutrients through gradual release of minerals that are bound in the C-structure (Lehmann et al., 2003b; Gundale and DeLuca, 2006).

Predictions and interpretations of soil processes in response to charcoal will benefit from enhanced knowledge of the patterns of natural variation in charcoal traits (Lehmann et al., 2011). In particular, little is known about the expected variability in the structural and chemical composition of charcoal and the factors driving the variability.

Most charcoal in natural environments is derived from woody material. Wood-derived charcoal properties vary among plant species due to interspecific variation in physical and chemical structures (Hellberg and Carcaillet, 2003; Keech et al., 2005; Verheijen et al., 2010). For instance, increased sorptive capacities were found for charcoal with large amounts of macro-pores and this observed variation in pore size distribution was attributed to differences in tissue composition of wood (Keech et al., 2005). In most cases the elementary macro structure of the original material is retained and remains identifiable. This capillary structure of wood may contribute to charcoal macro porosity (Downie et al., 2009). However, it is likely that within species charcoal properties vary depending on the conditions under which the charcoal has been formed, i.e., the fire conditions. It is assumed, that fire conditions affect the chemical composition of wood by volatilizing different inorganic and organic elements, while others are retained and become potentially bioavailable (Downie et al., 2009). Along

with this mass loss, microstructural rearrangement and volume reduction can occur during charcoal formation (Downie et al., 2009). The degree of physical changes in the charcoal material depends primarily on the maximum heating temperature, but also on the flame exposure time. The period of exposure determines the vapor phase residence time (Antal and Gronli, 2003). Thus, some volatile matter may not be converted to a gaseous or liquid phase, but rather react further with the carbonaceous material to build so-called secondary charcoal. This may lead to a loss of structural complexity. Additionally, flame residence time determines how fast heat is transferred and if a reaction can be completed (Downie et al., 2009). Thus, transitions in the carbon-based structure of charcoal were observed at higher temperatures for short retention times, but at lower temperatures for long retention times (Amonette et al., 2009). Charcoal that is formed at high temperatures tends to have increased sorptive capacities (Gundale and DeLuca, 2006) which may be related to increased surface areas at high temperatures (Glaser et al., 2002). Pore structure, surface area and adsorption capacities were found to change considerably due to high peak temperatures in combination with long retention times (Antal and Gronli, 2003; Downie et al., 2009). Depending on the maximum temperature, certain elements reach their melting points or are just released to the atmosphere. The relative proportion of these elements varies with species and, hence, will influence the degree of modification in the original botanical structure. Thus, the final composition/quality (amount of volatile matter) of charcoal likely depends on both fire conditions and species origin (Chan et al., 2009; Downie et al., 2009; Gundale and De Luca, 2006).

It is therefore to be expected that for some traits the temperature range under which changes occur is species-specific. Such interaction effects have rarely been addressed (Baldrock and Smernick, 2002; Pastor-Villegas et al., 2007; Gaskin et al., 2008). Moreover, the variation in physical charcoal traits is usually assumed to be driven by differences among plant species (Verheijen et al., 2010), but still little is known about the importance of intraspecific variation in charcoal properties (related to the fire conditions under which the charcoal is formed) relative to interspecific variation. While it has been widely accepted to use surrogates (activated carbon) in order to represent natural charcoal (Zackrisson et al., 1996; Wardle et al., 1998; Keech et al., 2005) and its trait variability (Gundale and De Luca, 2006), only few studies have tested inter- and intraspecific charcoal trait variability under natural fire conditions (Hille and den Ouden, 2005; Brown et al., 2006).

To infer how trait variability could influence charcoal effects on ecological processes relevant to the carbon cycle, the specific aim of this study is to determine the range of inter- and intraspecific trait variability in charcoal produced by different woody species. Thus, we simulated the natural charring process in a controlled experiment and determined the effect of species, temperature and residence time on charcoal characteristics including pH, EC, PO_4^{3-} , NH_4^+ , NO_3^- , porosity and pore size distribution. Moreover, we analyzed the same key charcoal properties of wildfire produced charcoal in comparison to artificially made charcoal using the same wood. It might be that some charcoal traits primarily depend on wood species, while other traits primarily depend on the fire conditions. Furthermore, an interaction effect of species and environmental conditions on charcoal traits could be expected. The null

hypothesis would be that neither wood species nor fire conditions explain variability in charcoal traits. Specifically, I asked the following question:

To what extent is the total variation in charcoal traits distributed between species and fire conditions or their interactions?

2. Material and Methods

2.1 Species selection

For the experiments we selected three common boreal tree species: *Betula pendula* Roth, *Pinus sylvestris* L., and *Sorbus aucuparia* L. (hereafter referred to as *Betula*, *Pinus*, and *Sorbus*). We collected wood fragments not larger than 1 cm in diameter from living trees at a forest site in Umeå, Northern Sweden. *Pinus sylvestris* is the second most widespread and abundant coniferous tree species in Northern boreal forests. In the first decades after fire, it often occurs together with *Betula pendula* (as well as *Betula pubescens*), and occasionally *Sorbus aucuparia* (Hellberg, 2004). Moreover, the choice of the species was based on a previous study (Pluchon et al., in prep.) testing for the effects of charcoal (derived from nine boreal tree species) on tree seedling growth. *Sorbus* and *Betula*-derived charcoal showed strong positive effects on the growth of *Betula pendula*, *Populus tremula*, *Pinus sylvestris* and *Picea abies* seedlings.

2.2 Charcoal production

Experiment 1: Barrel method (three temperatures)

The aim of experiment 1 was to test the influence of fire conditions and species origin on the variability of charcoal traits. We performed a barrel experiment manipulating 1) charcoal species, 2) flame temperature, and 3) flame residence time (defined as the time of combustion in visible flames). Charcoal was produced under controlled and reproducible conditions using an isolated gas flame (propane gas) (Fig. S3). Due to fluctuations in gas flame intensity it was necessary to obtain an average thermocouple reading for each treatment temperature. A variation of ± 100 °C could not be avoided; therefore, we selected treatment temperatures which differed about 200 °C (see appendix: thermocouple data). Selection of temperatures and time was based on observations during a prescribed fire (see below). The maximum temperature was set at 900 °C with residence times of 5, 10 and 15 minutes. An intermediate temperature was set at 700 °C for 5, 10 and 15 minutes. A residence time of 5 minutes at 700 °C, however, appeared to be a too short exposure time to produce fully charred materials. The lower temperature we selected was 450 degrees C, which corresponds to the typical temperatures of low intensity surface fires (see appendix Fig. S2) (Wiedemann et al., 1988, Chandler et al., 1991). At 450 °C, a residence time of 45 min was necessary to produce fully charred material. Hence, the design was an unbalanced split-split plot design with three species, i.e. *Sorbus*, *Betula* and *Pinus*, three temperatures, i.e. 450 °C, 700 °C and 900 °C, and varying resident times. Each of the 18 treatments was replicated five times, except for the treatment of 450 °C which was replicated two times (because of time constraints and budgetary reasons). Before the charring process, the collected wood pieces were oven-dried (60 °C) for 24 hours to exclude differences in moisture content, which have been shown to influence the charring process (Schmidt and Noack, 2000). Wood samples were wrapped in a thin sheet of aluminum (see appendix Fig. S2) to simulate the low oxygen/inert conditions that are essential in the charring process.

Experiment 2: Barrel - Muffle furnace (One temperature)

The aim of experiment 2 was to compare the low temperature charcoal (450 °C) from experiment 1 with charcoal produced at 450°C in a muffle furnace (Pluchon in prep.), a commonly used method to create biologically active charcoal (e.g. Wardle et al., 1998; Zackrisson et al., 1996; Keech et al., 2005; Pluchon in prep.). This comparison was required in order to validate our newly developed barrel method (low oxygen conditions and control of flaming combustion). Further, Brown et al. (2006) argued that new methods (such as the barrel method) are needed to more adequately describe natural charcoal formation. The muffle furnace technique only provides electronically heat, whereas the barrel method simulates a more natural heat transfer from a flame. Hence, wood fragments were collected in the same way as described above. In order to keep low oxygen conditions during the formation of charcoal in the muffle furnace, wood fragments were covered with sand in an aluminum container at 450°C for 45 minutes.

Experiment 3: Barrel - Wildfire (One temperature)

The aim of experiment 3 was to compare experimentally-produced charcoal (experiments 1 and 2) with naturally produced charcoal. In experiment 3, we focused exclusively on *Pinus*. Naturally produced charcoal was collected during a prescribed burn at a forest site 70 km west of Umeå (Käringsberget). At the 10 ha site, we randomly selected five individual logs from *Pinus*. Dead trees were chosen, because of the higher probability to produce charcoal. Where large branches are piled, areas of low oxygen availability exist, which is crucial for incomplete combustion. For each of the five logs, one 1 m² observational area was established. In each of these areas, the following procedure was applied: (1) Before the fire, unburned wood was collected for later use in a barrel experiment; (2) flame residence time was recorded; (3) after the fire, charcoal was collected. Additionally, two observation areas were equipped with a thermocouple to record temperatures during the charring process (see appendix Fig. S2). The unburned wood (from step 1) was treated as described above (experiment 1), except that the temperature treatment consisted only of one temperature (e.g. 900 °C) in order to compare it to the highest temperature that was recorded during the wildfire (see appendix Fig. S2).

2.3 Charcoal characterization

The following analyses were performed for all experiments (see above).

Microscopy design: Transversal porosity and pore size distribution

Charcoal porosity is determined as the total volume of pores over the total volume of charred material. Here, porosity was estimated using transversal porosity, which is an accurate estimation of charcoal porosity (Keech et al. 2005). It uses a cross-sectional area of the charcoal sample to create a two dimensional image. The area covered by pores is then calculated. The ratio between the pore area and the total area of the two dimensional image relates to the total porosity. A high ratio reflects a high porosity. Pores included in this study, consist of tracheids for *Pinus*, and of vessels, fibers and axial parenchyma for *Betula* and *Sorbus*. Lehmann et al. (2009) distinguished between micro-pores ($\varnothing < 2$ nm), meso-pores ($\varnothing > 2$ nm- < 50 nm) and macro-pores (> 50 nm). In our study, all pore sizes were > 50 nm. These macro pores has shown to have vital functions in soils like aeration, water retention and are also habitats for a wide range of microbes (Lehmann et al., 2009). The smallest recorded pore diameter was 248, 5 nm. Therefore, we distinguished between the following pore size classes: micro-pores ($< 50 \mu\text{m}^2$), meso-pores ($> 50 \mu\text{m}^2$ and $< 250 \mu\text{m}^2$), and macro-pores ($> 250 \mu\text{m}^2$) (Keech et al., 2005). Wildman et al. (1991) classified macro-pores into similar groups, comparing them to size classes of silt and sand particles.

A microtome (Leitz 1512) was used to obtain transversal sections of the raw charcoal samples. A standard rotary microtome, with a blade angle of 10-15 degree was applied and the sections were cut 10 μm thick, at -20 °C. Before sectioning, each charcoal piece was dropped into freezing medium with optimal cutting temperature (i.e. .3 O.C.T. compound) to allow the cryomicrotomy technique. To facilitate the insertion of the medium, we applied an intermediary step, replacing the air in the charcoal's cavities by water (using a vacuum pump).

All charcoal sections were examined using a Leica DM LB2 light microscope (Leica Microsystems, Wetzlar, Germany). Images were captured using a digital Leica DFC 425 C camera. A magnification of 20x was used to acquire images of a representative observation area of 2622 mm^2 . This area included at least one growth ring, which was distinctively recognizable in all charcoal types (Schweingruber, 1990) (Fig.1).

The analyses and anatomical measurements of the light microscope pictures were done using the software Image J version IJ 1.45 M. To distinguish between pore and cell wall area, a threshold was set manually based on the image grey-level range. Then the grey scaled microscope images were converted into binary images. As illustrated in Fig. 1, the pore area becomes black and the cell walls white. First, all threshold images were measured for transversal porosity, which is the total pore area of charcoal (cm^2 per cm^2 charcoal). Transversal porosity analyses were performed on the entire image. Second, the pore size distribution was calculated as the proportion of each pore size class of the transversal area.

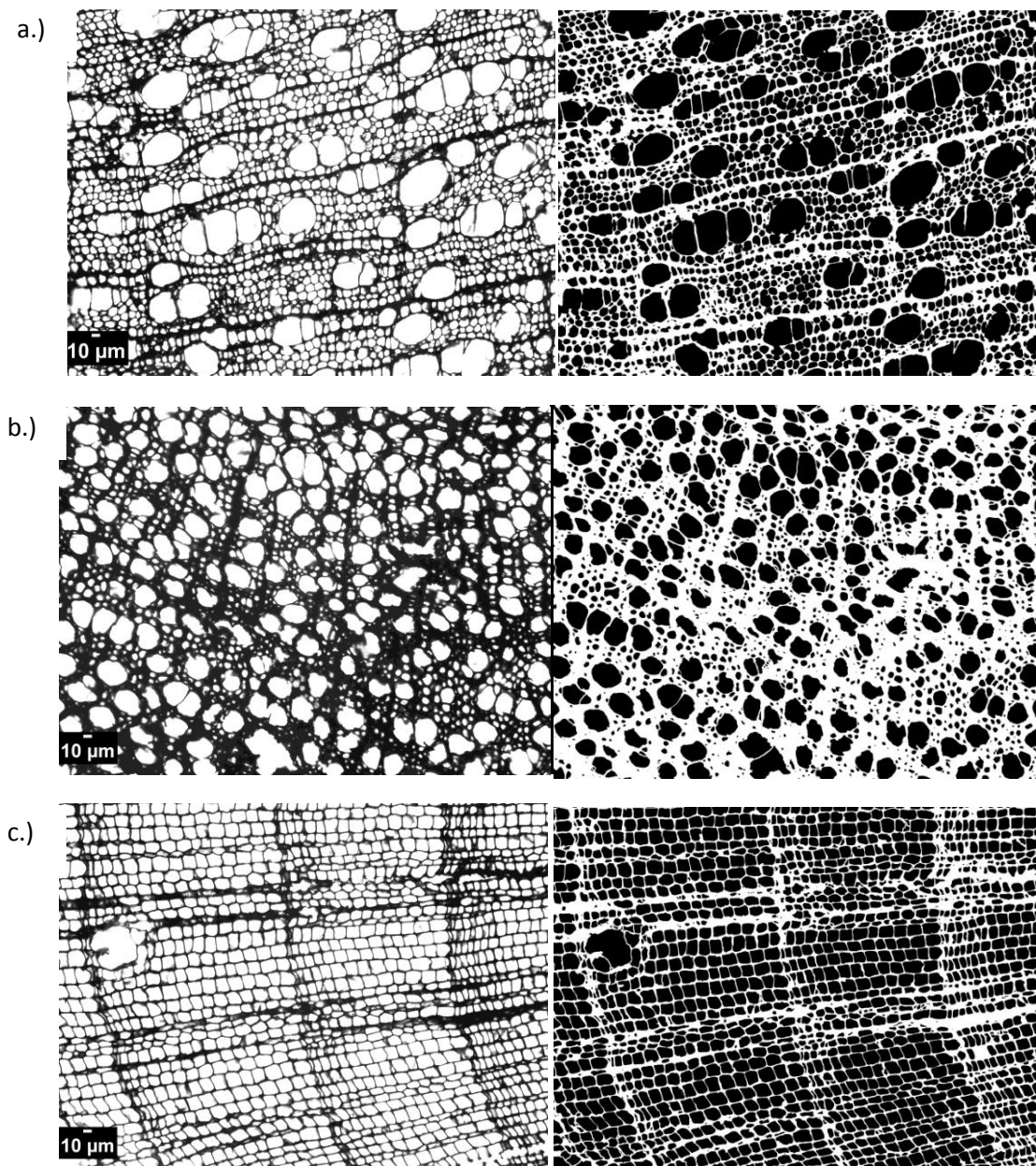


Figure 1: Light microscope pictures (left) and threshold image (right) of transversal sections of wood charcoal for a) *Betula*, b) *Sorbus*, and c) *Pinus*. Microscope pictures and threshold images are at the same scale and magnification (20x).

Laboratory analysis

Charcoal samples were divided into sub-samples to determine: 1) pH, 2) electric conductivity, 3) NO_3^- , PO_4^{3-} , NH_4^+ , and 4) bulk density. The pH was measured in a 1:5 solution (by weight) of sieved charcoal (<4mm) and distilled water was used when measuring the pH with a standard silver chloride electrode. Electric conductivity was measured using a pure water meter (YK-30WA) in a 1:15 solution (by weight) of sieved charcoal (<4mm) and distilled water. To measure inorganic N and P, charcoal was sieved (<4mm), extracted with KCl, and analyzed for NH_4^+ , NO_3^- and PO_4^{3-} . One g of charcoal was mixed with 5 ml 1M KCl and shaken for 1 h. A centrifuge was used to separate the solid charcoal material from the liquid solution (5 min, 3000 t/s). This solution was then filtrated through Whatman filters, prior to

analyzing the extractants on an air-segmented continuous flow-analyzer (Auto analyzer III, Norderstedt, Germany). Density measurements were conducted by measuring the dry weight of the raw charcoal pieces and thereafter the volume displacement in deionized water (De Luca and Gundale, 2006).

2.4 Statistical analysis

Experiment 1: Four out of the ten variables (EC, density, transversal porosity) analyzed met the assumptions of normality and homogeneity of variance, and two additional variables (PO_4^{3-} , micro porosity) met the assumptions after square root-transformations. These five variables were analyzed using analysis of variance with “species” (*Betula*, *Pinus*, *Sorbus*), “temperature” (450°C, 700°C, 900°C) and “time” (5, 10, 15 and 45 min) as fixed factors and “block” (five replicates) as a random factor. To detect significant differences among treatment means/between groups Tukey’s post-hoc tests were used ($p < 0.05$). The remaining variables were analyzed using non-parametric Kruskal-Wallis tests, followed by pairwise Mann-Whitney U tests to determine pairwise differences among main factors (i.e. species, temperature, time).

Experiment 2: Seven out of ten variables (density, porosity, macro porosity, meso porosity, micro porosity, pH, EC) met the assumptions of normality and homogeneity of variance. These variables were tested using general linear models with “species” (*Betula*, *Pinus*, *Sorbus*) and “charring process” (muffle furnace, barrel) as fixed factors. The remaining parameters (NO_3^- , PO_4^{3-} , NH_4^+) could not be transformed and were analyzed using Kruskal-Wallis tests.

Experiment 3: Six out of ten variables (bulk density, porosity, meso porosity, micro porosity, EC, pH) met the assumptions of normality and homogeneity of variance. These variables were tested using general linear models with “charring process” (wildfire, barrel) and “residence time” (5, 10, 15 min) as fixed factors. Three non-normal distributed variables (NO_3^- , PO_4^{3-} , NH_4^+) could not be transformed and were analyzed using a Kruskal-Wallis test. In case of significant differences among treatment means, pairwise Mann-Whitney U tests were used.

All statistical analyses were performed using Minitab 16 statistical software (2010).

3. Results

3.1. Experiment 1: Barrel method (three temperatures)

Charcoal traits differed among species, fire conditions, and their interactions under the controlled environmental conditions in a barrel. Species and temperature influenced the charcoal traits electric conductivity, transversal porosity, density and pH. Moreover, except for pH, species \times temperature interactions were shown for all of these variables.

Charcoal electric conductivity, indicating the total amount of soluble salts in charcoal, significantly differed among species (ANOVA: $F_{2,77} = 11.59$; $P < 0.001$; Table 1) and by temperature (ANOVA: $F_{2,77} = 35.32$; $P < 0.001$; Table 1). However, the significant species \times temperature interaction (ANOVA: $F_{4,77} = 4.94$; $P < 0.01$; Table 1) indicates that species and temperature effects were dependent on each other (Figure 2). Charcoal electric conductivity was not affected by residence time. The values for electric conductivity were about 36% higher at 900°C than at 450 and 700°C. On average, *Sorbus* showed 33% higher values compared to *Betula* and *Pinus*. Generally, highest values for electric conductivity were observed for charcoal produced at 900°C. The temperature effect was strongest for *Pinus* and *Sorbus*, with significantly higher values at 900°C than at 450 °C and 700 °C (52% and 39%, resp.). At 450°C, no species effects were found. At 700°C, the values for electric conductivity were significantly higher for *Sorbus* than for *Pinus*; values for *Betula* were intermediate and did not significantly differ from *Sorbus* and/or *Pinus*. At 900°C, the values were lowest for *Betula*, and did not differ between *Sorbus* and *Pinus*.

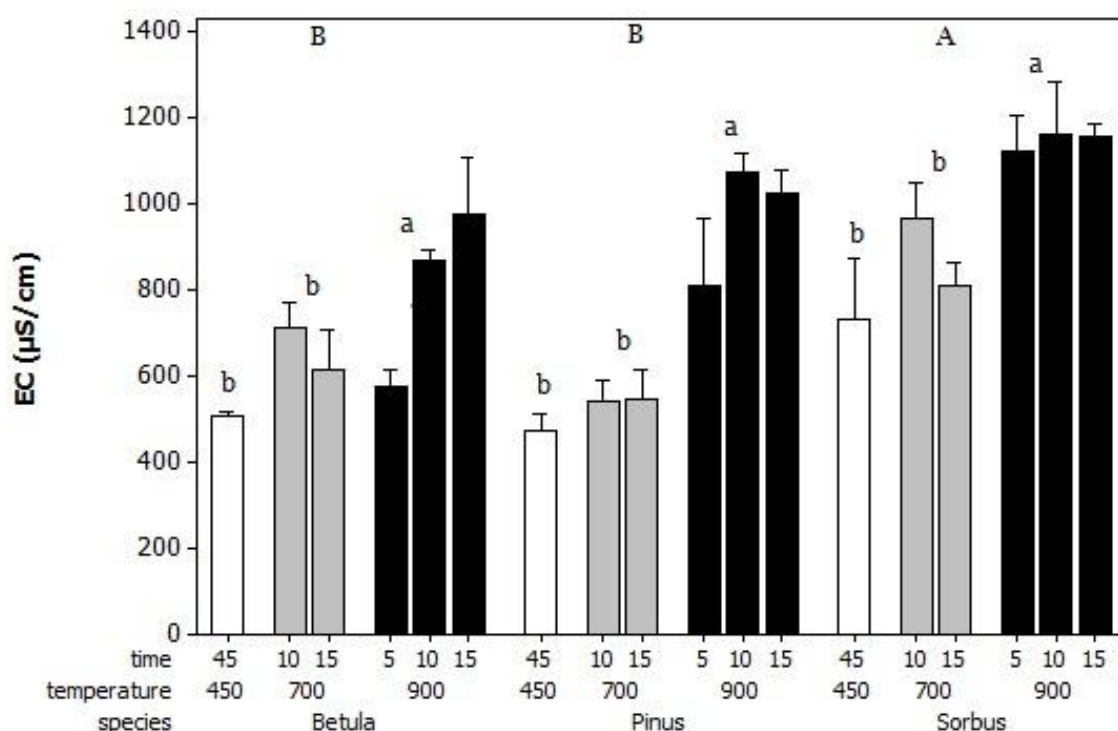


Figure 2: Electric conductivity (EC) of charcoal made from *Betula*, *Pinus* and *Sorbus* at 450°C for 45 min, at 700°C for 10 and 15 min and at 900°C for 5, 10 and 15 min. Data were analyzed using general linear models. Significance was tested for species, temperature, time and all possible interactions between these factors (Table 1). Bar groups (e.g. *Betula*, *Pinus*, *Sorbus*) having different uppercase letters or bars shaded differently among groups having different lowercase letters are significantly different at $P < 0.05$. Shown are mean \pm s.e.

Charcoal bulk density was also affected by species (ANOVA: $F_{2,80} = 33.25$; $P < 0.001$; Table 1) and by temperature (ANOVA: $F_{2,80} = 9.76$; $P < 0.001$; Table 1), and there was a significant interaction species \times temperature interaction (ANOVA: $F_{4,80} = 2.89$; $P < 0.05$; Table 1; Figure 3). Charcoal bulk density was not affected by residence time. Overall, charcoal bulk density was significantly lower for *Pinus* than for *Betula* and *Sorbus* ($< 10\%$). For all species, charcoal bulk density was significantly higher at 450 °C than at 700 °C and 900 °C ($> 10\%$). For *Betula*, charcoal bulk density was significantly higher at 450°C than at 700 °C and

900°C, while for *Pinus* and *Sorbus* charcoal density was unaffected by temperature.

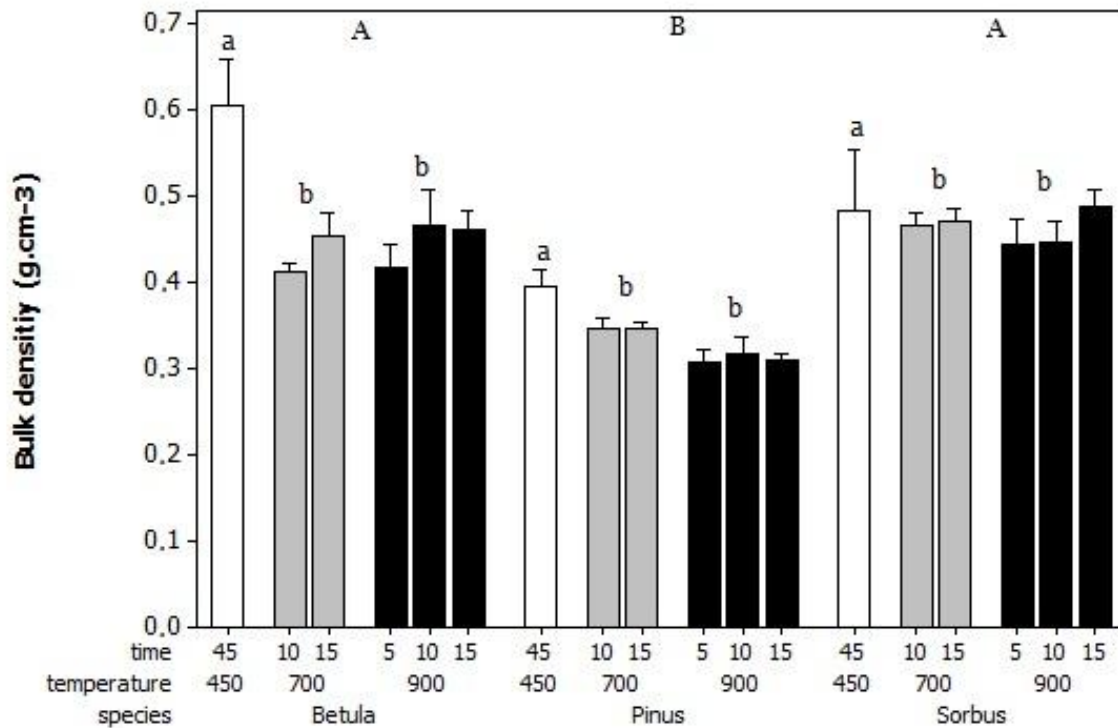


Figure 3: Bulk density of charcoal made from *Betula*, *Pinus* and *Sorbus* at 450°C for 45 min, at 700°C for 10 and 15 min and at 900°C for 5, 10 and 15 min. Data were analyzed using general linear models. Significance was tested for species, temperature, time and all possible interactions between these factors (Table 1). Bar groups (e.g. *Betula*, *Pinus*, *Sorbus*) having different uppercase letters or bars shaded differently among groups having different lowercase letters are significantly different at $P < 0.05$. Shown are mean \pm s.e.

Transversal porosity was also affected by species (ANOVA: $F_{2,69} = 7.15$; $P < 0.05$; Table 1), temperature (ANOVA: $F_{2,69} = 4.07$; $P < 0.05$; Table 1) and their interaction (ANOVA: $F_{4,69} = 2.88$; $P < 0.05$; Table 1; Figure 4). Species explained more of the variation in transversal porosity than did temperature. Overall, *Sorbus* showed significantly lower values for transversal porosity ($< 10\%$) compared to *Betula* and *Pinus*. The interaction effect demonstrated that at 700°C, transversal porosity was significantly higher for charcoal made from *Pinus* than for charcoal made from *Betula* or *Sorbus*. At 450°C and 900°C transversal porosity did not differ among species.

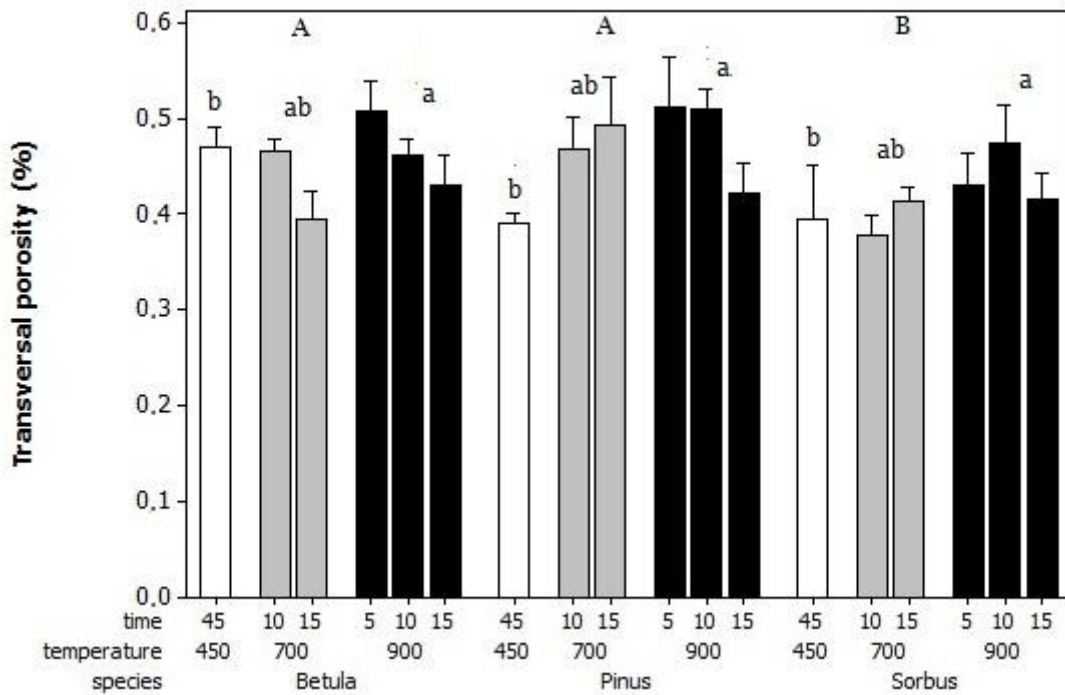


Figure 4: Transversal porosity of charcoal made from *Betula*, *Pinus* and *Sorbus* at 450°C for 45 min, at 700°C for 10 and 15 min and at 900°C for 5, 10 and 15 min. Data were analyzed using general linear models. Significance was tested for species, temperature, time and all possible interactions between these factors (Table 1). Bar groups (e.g. *Betula*, *Pinus*, *Sorbus*) having different uppercase letters or bars shaded differently among groups having different lowercase letters are significantly different at $P < 0.05$. Shown are mean \pm s.e.

Charcoal pH was affected by temperature (Kruskall-Wallis, $H = 21.24$, $DF = 2$, $p < 0.001$; Table 1) and residence time (Kruskall-Wallis, $H = 19.12$, $DF = 3$, $p < 0.001$, Table 1), but not by species (Kruskall-Wallis, $H = 4.79$, $DF = 3$, $p = 0.09$, Table 1) (Figure 5). pH values were consistently higher at 900 °C than at 700 °C ($> 8\%$) and 450°C ($> 22\%$). Furthermore, charcoal pH was significantly higher 700°C than at 450°C ($> 14\%$). A flame residence time of 15 min increased the pH by 12% compared to a residence time of 5 min. In addition, residence times of 10 min compared to 5 min increased the charcoal pH significantly ($> 10\%$).

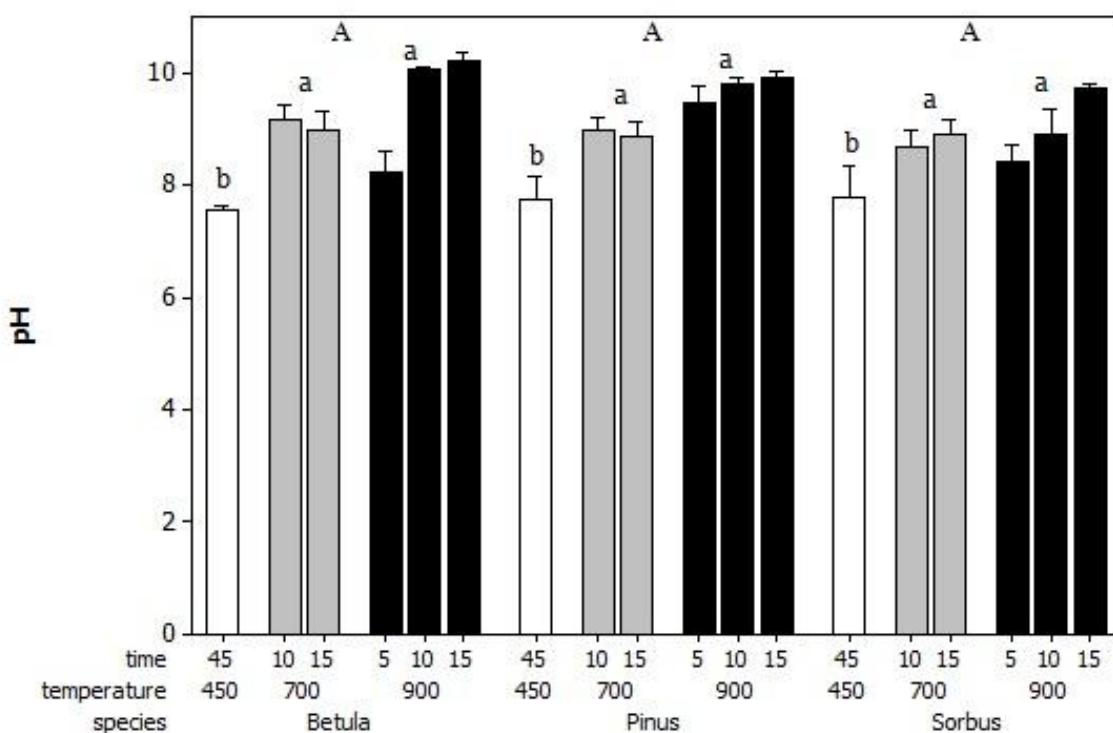


Figure 5: Measurements done of pH in charcoal made from *Betula*, *Pinus* and *Sorbus* at 450°C for 45 min, at 700°C for 10 and 15 min and at 900°C for 5, 10 and 15 min. Data were analyzed using general linear models. Significance was tested for species, temperature, time and all possible interactions between these factors (Table 1). Bar groups (e.g. *Betula*, *Pinus*, *Sorbus*) having different uppercase letters or bars shaded differently among groups having different lowercase letters are significantly different at $P < 0.05$. Shown are mean \pm s.e.

No significant effect of species and treatment were found for PO_4^{3-} concentration in charcoal. However, PO_4^{3-} concentrations were slightly higher in charcoal from *Betula* and *Sorbus* than in charcoal from *Pinus* (Figure 7a; Table 1). In contrast to PO_4^{3-} concentration, NO_3^- concentration was affected by temperature (Kruskall-Wallis, $H = 6.72$, $DF = 2$, $p < 0.05$; Table 2; Figure 7b), 900°C and 700°C exhibited a significant difference compared with 450°C, however NO_3^- showed not to be dependent upon species. NH_4^+ concentrations in charcoal were strongly affected by temperature (Kruskall-Wallis, $H = 16.66$, $DF = 2$, $p < 0.001$; Table 2) and residence time (Kruskall-Wallis, $H = 15.51$, $DF = 3$, $p < 0.01$; Table 2; Figure 7c). NH_4^+ concentrations were significantly higher at 450 °C than at 700 °C and 900 °C (i.e. 98%). And, NH_4^+ concentrations were significantly higher when charcoal was produced at a residence time of 45 min than at a residence time of 5, 10 and 15 min.

Charcoal pore size distribution varied among species, but was not affected by temperature, and residence time. The proportion of micro pore area per transversal pore area (hereafter referred to as micro porosity) was highest for *Betula* (i.e. 20%) ANOVA: $F_{2,72} = 22.10$; $P < 0.001$; Table 1; Figure 6, resp. Figure 7d) *Pinus* charcoal had the highest relative amount of meso pores (i.e. 74%) (Kruskall-Wallis, $H = 52.68$, $DF = 2$, $p < 0.001$; Table 2; Figure 6, resp. Figure 7e); meso porosity was higher for *Pinus* than for *Betula* and *Sorbus*. *Sorbus* charcoal had the highest relative amount of macro pores (i.e., 66%); macro porosity was higher for *Sorbus* than for *Betula* and *Pinus* (Kruskall-Wallis, $H = 56.17$, $DF = 2$, $p < 0.001$; Table 2;

Figure 6, resp. Figure 7f). Additionally macroporosity was significantly higher for *Betula* than for *Pinus*.

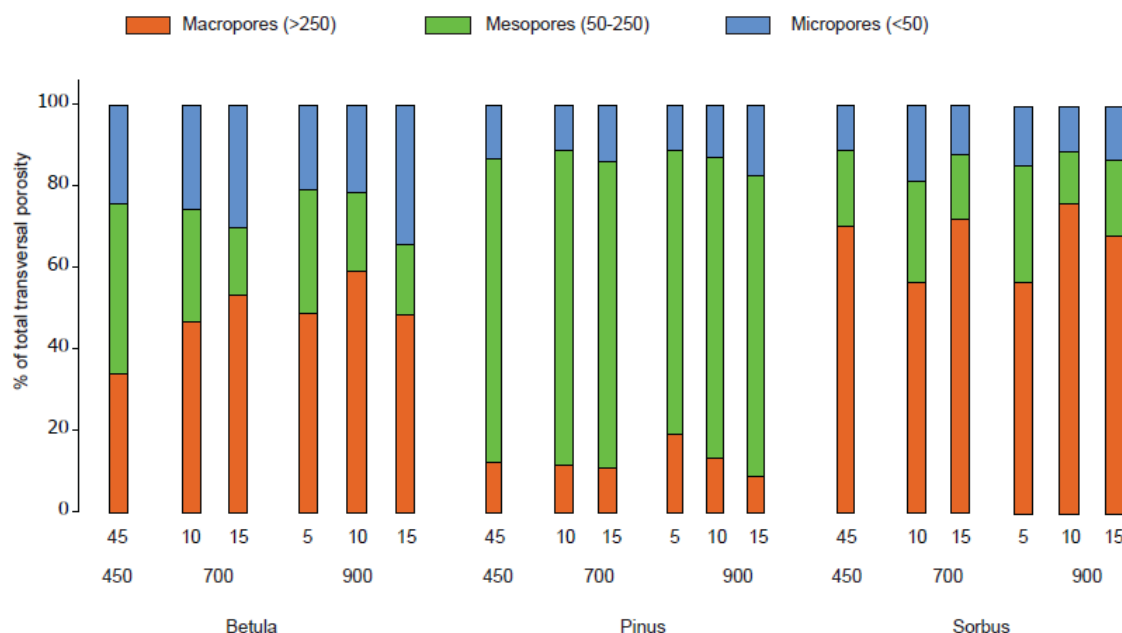


Figure 6: The pore size distributions for the three species (*Betula*, *Pinus* and *Sorbus*) are illustrated as the percentage of total number of transversal pores. The intervals are micro pores (<50 μm²), meso pores (50-250 μm²) and macro pores (>250 μm²). Data were analyzed using general linear models. Significance was tested for species, temperature, time and all possible interactions between these factors (Table 1 and Table 2).

Table 1 Experiment 1: General linear model (Anova) testing effects of species (*Betula*, *Sorbus*, *Pinus*), temperature (450°C, 700°C and 900°C), and residence time (5, 10, 15 and 45 min) and their interactions on normal distributed charcoal traits (Electric conductivity (EC), PO₄³⁻, Bulk density, Transversal porosity, Micro porosity).

	EC (μS/cm)			PO ₄ ³⁻ (mg/l)		Density (g cm-3)		Transversal porosity (%)		Micro porosity (%)	
	d.f.	F	P-value	F	P-value	F	P-value	F	P-value	F	P-value
Species	2	11.59	< 0.001***	2.78	0.069	33.25	< 0.001***	7.15	< 0.01**	22.10	< 0.001***
Temperature	2	35.32	< 0.001***	2.15	0.124	9.76	< 0.01**	4.07	< 0.05*	0.84	0.43
Time	3	2.30	0.084	0.22	0.884	2.63	0.056	2.45	0.069	1.16	0.332
Species x temperature	4	4.94	< 0.01**	0.36	0.839	2.89	< 0.05*	2.88	< 0.05*	0.48	0.75
Error (mean squares)	80	0.55		0.36		0.53		0.27		0.40	

* Indicates significant effect

Table 2 Experiment 1: Kruskal-Wallis statistics testing effects of species (*Betula*, *Sorbus*, *Pinus*), temperature (450°C, 700°C and 900°C), and residence time (5, 10, 15 and 45 min) on non-normal distributed charcoal traits (pH, NO_3^- , NH_4^+ , Macro porosity, Meso porosity).

		pH		NO_3^- (mg/l)		NH_4^+ (mg/l)		Macro porosity (%)		Meso porosity (%)	
	d.f.	K-W	P-value	K-W	P-value	K-W	P-value	K-W	P-value	K-W	P-value
Species	3	4.79	0.09	1.72	0.42	0.15	0.92	56.17	< 0.001***	52.68	< 0.001***
Temperature	3	21.24	< 0.001***	6.72	< 0.05*	16.66	< 0.001***	0.17	0.91	0.09	0.95
Residence time	3	19.12	< 0.001***	4.36	0.23	15.51	< 0.01**	0.18	0.97	2.917	0.39
Error (mean squares)	80										

* Indicates significant effect

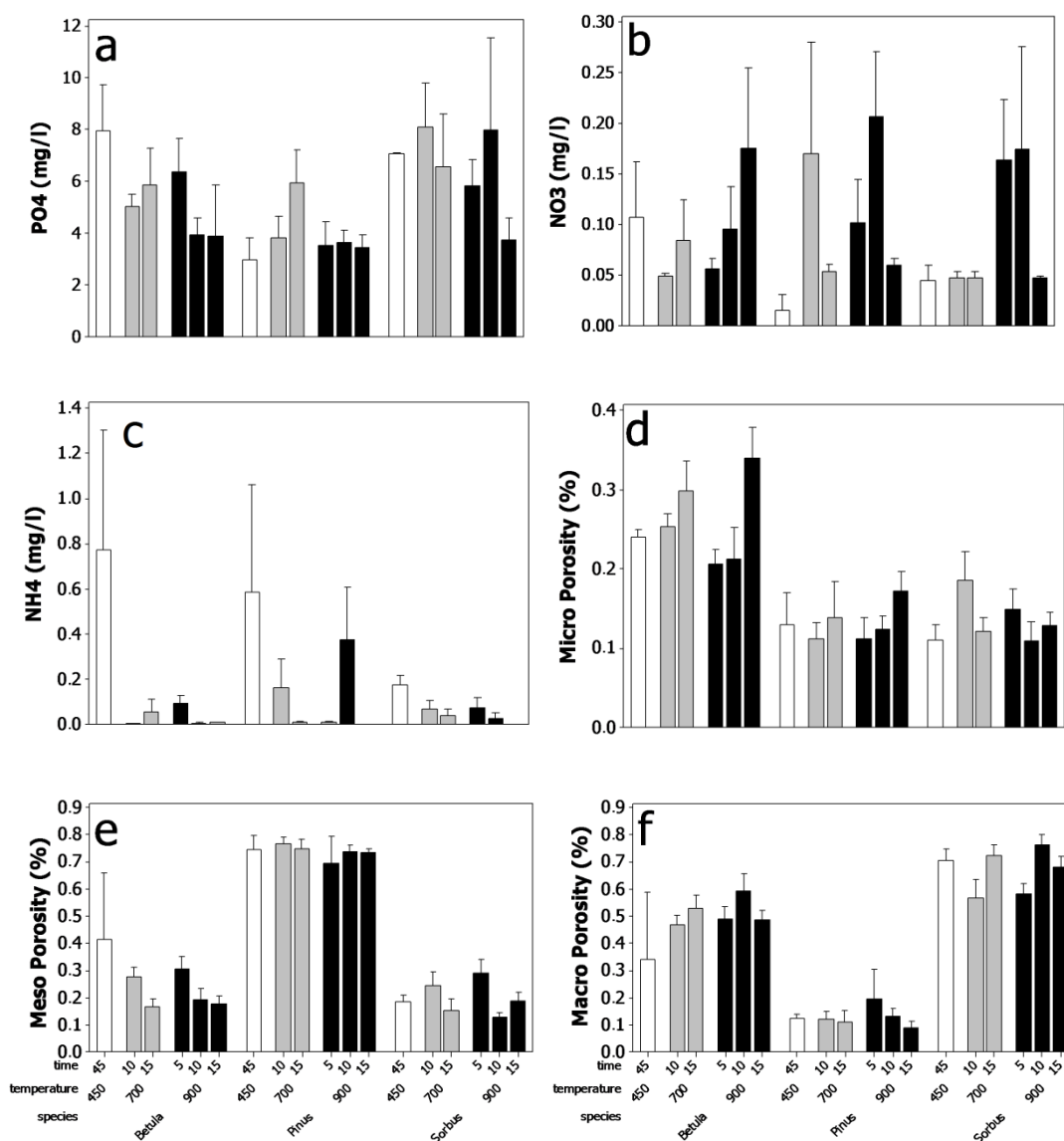


Figure 7: PO_4^{3-} (a), NO_3^- (b); NH_4^+ (c); micro porosity (d), meso porosity (e) and macro porosity (f) of charcoal made from *Betula*, *Pinus* and *Sorbus* at 450°C for 45 min, at 700°C for 10 and 15 min and at 900°C for 5, 10 and 15 min. Data were analyzed using non parametric Kruskal- Wallis test (KW) (Table 2). Shown are mean \pm s.e.

3.2 Experiment 2: Barrel - Muffle furnace (One temperature)

There was no significant difference between furnace-made charcoal and charcoal produced in a barrel. However, for several charcoal traits significant species effects were shown. Electric conductivity (EC) was higher for *Sorbus* charcoal than for *Pinus* charcoal (ANOVA: $F_{2,10}=6.03$; $P<0.05$; Figure 8a). Charcoal bulk density was lower for *Pinus* charcoal than for *Betula* and *Sorbus* charcoal (ANOVA: $F_{2,10}=6.68$; $P<0.05$; Figure 8b). Meso porosity was higher for *Pinus* charcoal than for charcoal (ANOVA: $F_{2,10}=6.98$; $P<0.05$; Figure 8c), while macro porosity was higher for *Sorbus* charcoal than for *Pinus* charcoal (ANOVA: $F_{2,10}=6.74$; $P<0.05$; Figure 8d). Micro porosity (Figure 8j), transversal porosity (Figure 8e), pH (Figure 8f) and charcoal nutrient concentrations (i.e. extractable PO_4^{3-} , NO_3^- , and NH_4^+) (Figure 8g, 8h, 8i,) did not differ between species.

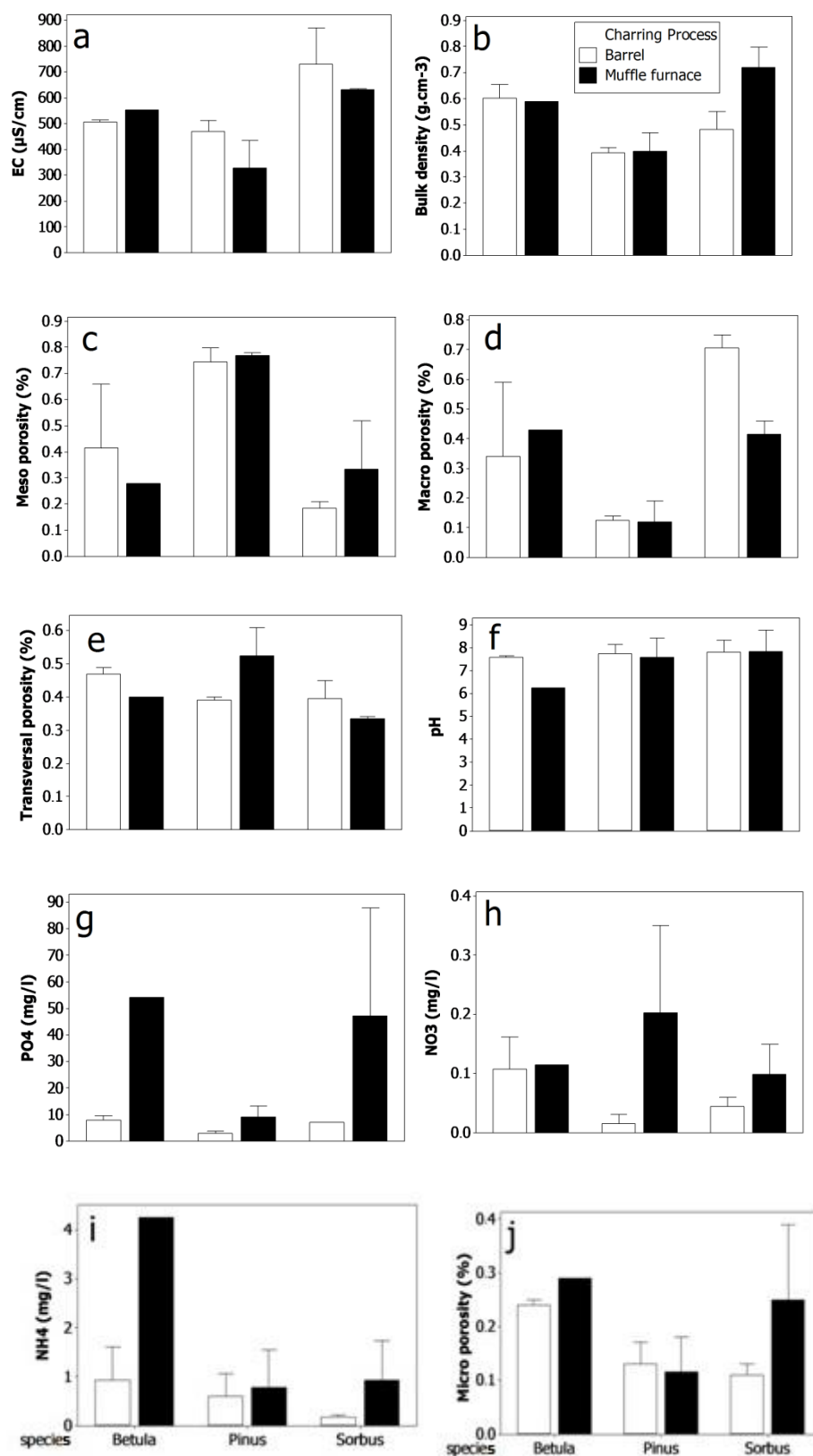


Figure 8: Electric conductivity (EC) (a), bulk density (b), meso porosity (c), macro porosity (d), transversal porosity (e), pH (f), PO_4^{3-} (g), NO_3^- (h), NH_4^+ (i) and micro porosity (j) of charcoal made at 450°C from *Betula*, *Pinus* and *Sorbus* under two different charring processes, i.e. in a barrel and in a muffle furnace. Shown are mean \pm s.e.

3.3 Experiment 3: Barrel - Wildfire (One temperature)

Electric conductivity (EC) was significantly higher for pine charcoal formed under controlled conditions in a barrel than for pine charcoal formed under wildfire conditions (i.e., 74%) (ANOVA: $F_{1,19} = 8.66$; $P < 0.05$; Figure 9a). Charcoal pH was also significantly affected by the charring processes. The pH was higher when charcoal was produced under controlled conditions in a barrel than under wildfire conditions (i.e. 9%) (ANOVA: $F_{1,19} = 14.62$; $P < 0.01$). For pH, we also found a significant time \times charring process interaction (ANOVA: $F_{2,19} = 5.20$; $P < 0.05$; Figure 9b). For barrel-made charcoal, pH was higher at residence times of 10 and 15 than at a residence time of 5min, while for charcoal produced on wildfire condition pH was not affected by residence time. Charcoal PO_4^{3-} concentrations were higher for charcoal produced under wildfire conditions than for charcoal produced in a barrel (Kruskall-Wallis, $H = 5.77$, $DF = 1$, $p < 0.05$; Figure 9c). Charcoal bulk density (Figure 9d), pore size distribution and transversal porosity (Figures 9e, 9h, 9i, 9j), and concentrations of available N (Figure 9f and 9g) were not affected by charring conditions or residence time.

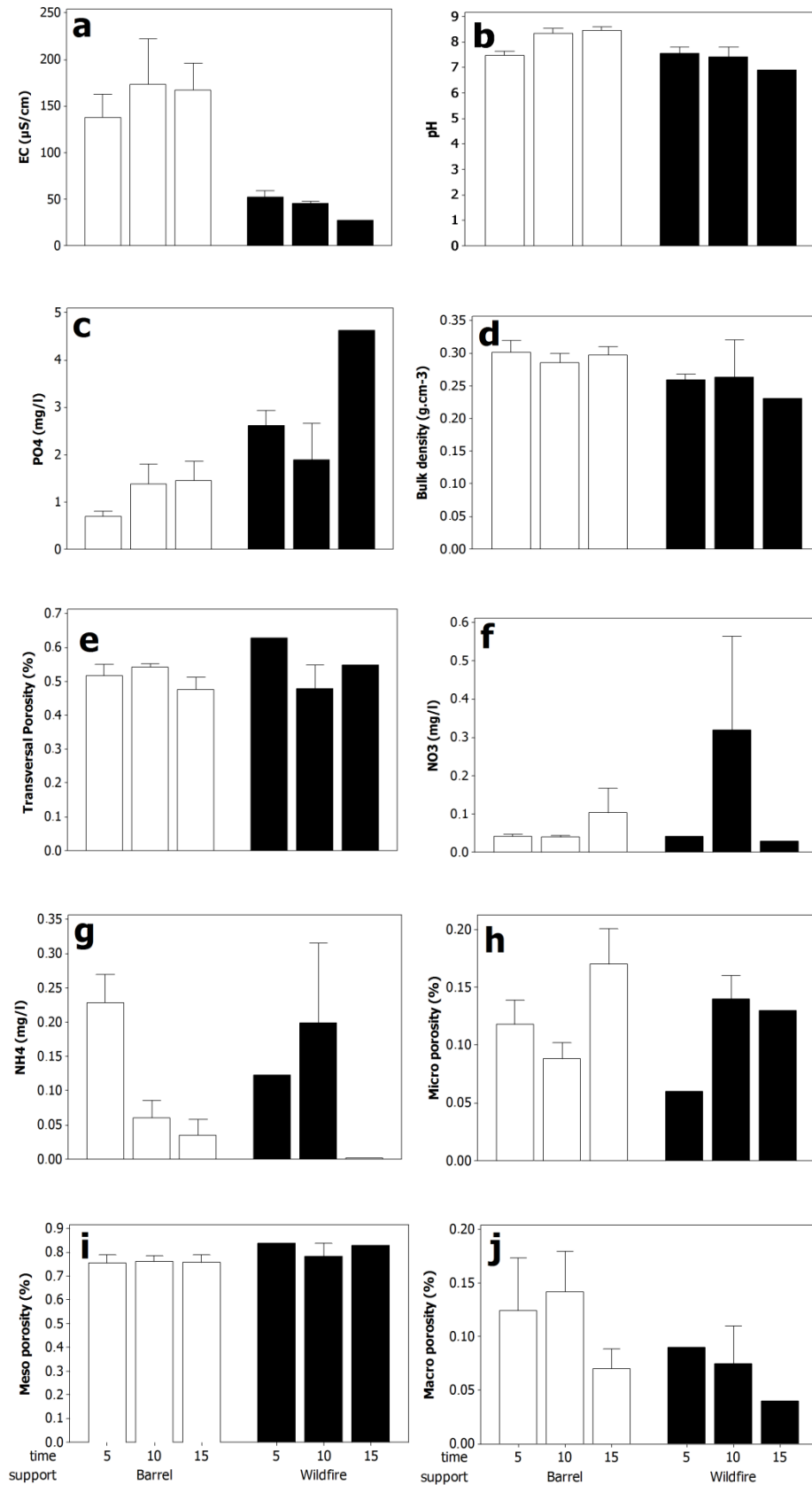


Figure 9: Electric conductivity (EC) (a), pH (b), PO₄³⁻ (c), bulk density (d), transversal porosity (e), NO₃⁻ (f), NH₄⁺ (g), micro porosity (h), meso porosity (i) and macro porosity (j) of charcoal made under two different charring processes, i.e. in a barrel at 900 °C for 5, 10 and 15min (white bars) and wildfire produced charcoal at three different residence times (black bars). Shown are mean \pm s.e.

4. Discussion

Experimental evidence in this study has shown that variation in charcoal properties caused by species and/or fire conditions may drive important ecological processes in boreal forest ecosystems. In the first experiment, we tested the variability of seven charcoal traits as a function of tree species (*Betula pendula*, *Pinus sylvestris*, *Sorbus aucuparia*), temperature (450 °C, 700°C, 900°C), flame residence times (5,10,15 and 45min) and, importantly, their interactions. In a second experiment, we examined the variability of the same charcoal traits for the above-mentioned tree species at one temperature (450°C), but under different charring process conditions (barrel vs muffle furnace). The third experiment was established to verify if the charcoal trait variability of *Pinus sylvestris* follows the same pattern under simulated conditions (i.e., a barrel method) as under wildfire conditions.

Our results demonstrated that the variability of three ecologically relevant charcoal traits, i.e., electric conductivity, transversal porosity, and bulk density were affected by the interactive effect of species and fire conditions. pH was by affected by the interactive effects of temperature and residence time. All other charcoal traits (PO_4^{3-} , NH_4^+ , NO_3^- and pore size distribution) were affected either by species or by fire conditions.

4.1. Experiment 1

In agreement with our hypothesis, charcoal trait variability could often be explained by a combination of factors (i.e., species and fire conditions). Moreover, for several traits, interaction effects were observed between species and fire conditions (in particular, temperature).

The increase of electric conductivity with temperature was strongly species dependent. This confirms previous findings by Gundale and De Luca (2006) who tested trait differences of charcoal made from wood and bark of *Pinus ponderosa* and *Psuedotsuga menziesii* at 350 °C and 800 °C. It has been suggested that at high temperatures base cations (i.e. Ca^{2+} , K^+ , Mg^{2+}) become more concentrated in charcoal pores (Bélanger et al, 2004; Gundale and De Luca, 2006). The higher concentration of soluble ions in *Sorbus* charcoal might be related to its intrinsic chemical tissue composition. Our study revealed that *Betula* and *Pinus* charcoal (e.g. wood) differ in their responses to temperature. It could be that different species are generating different amounts of ash residues with increasing temperatures. Specifically, *Pinus* showed a rapid increase in EC between 700°C and 900°C. Even though the general trend of the response of *Pinus* towards temperature was the same as for *Betula* and *Sorbus*, the magnitude of this response differed. This might be a function of the thermal stability of lignin which ceases to matter when reaching temperatures of 750°C and above (Downie et al., 2009). Therefore, one might argue that *Pinus* does not show a rapid increase until a temperature is reached where the thermal stability of lignin is lost and *Pinus* starts following similar trends as other species.

Soluble ions (i.e, NO_3^- , PO_4^{3-} , NH_4^+) were detected in all charcoal samples, indicating their resistance to leaching (Joseph et al., 2009); hence, this may constitute a potential long term

source of nutrients. Particularly charcoal made at high temperatures (i.e., 900 °C) could provide easily available nutrients for microbes and plants.

Charcoal bulk density was strongly affected by species. The higher density of *Sorbus* is most likely a function of its lower porosity compared to *Pinus* and *Betula*. This primarily results from the fact that the configuration of the starting material determines the degree of thermal alteration of the original pore structure. Species dependency for charcoal bulk density was also shown by Byrne and Nagle (1996), who predicted that density is linearly proportional to the density of the original plant material. Both, the cell diameter and the wall thickness determine the bulk density. Our values for bulk density ranged from 0.31 cm⁻³ to 0.48 cm⁻³, which correspond to the density values found by Byrne and Nagle (1996) (0.30 cm⁻³ and 0.43 cm⁻³). Downie et al. (2009) proposed that charcoal bulk density decreases with temperature, while porosity increases. Thus, an increase in temperature leads to volatilization of elements and to a more ordered, graphite-like carbon structure leaving voids behind.

In contrast to chemical charcoal traits, our results for transversal porosity show that the variability in structural charcoal traits may largely be explained by differences among species. Keech et al. (2005) produced charcoal from nine different species at 450°C with an average porosity of 57%, which is higher than our observed average of 43%; the discrepancy may be a result of the different species they used. We found particularly low porosity for *Sorbus* which could be associated with the high abundance of macro pores and a corresponding higher proportion of cell wall material. This structural characteristic showed to be imprinted in the charcoal structure of *Sorbus*. Additionally, an increase in temperature from 450 °C to 900 °C resulted in more pore space, probably due to devolatilization of inorganic and organic compounds and to the formation of an ordered structure of the charcoal (Downie et al., 2009). However, our data also indicate that the species respond differently to temperature. As such, transversal porosity of *Pinus* greatly increased with a rise in temperature from 450 °C to 900 °C, presumably resulting from the loss of cell material in the form of lignin. At 450°C, *Pinus* had the overall lowest transversal porosity. This is in agreement with Keech et al. (2005), who also showed that of all species *Pinus sylvestris* had the lowest transversal porosity at 450 °C. This trend might be related to the thick late wood characteristics of *Pinus* (Keech et al., 2005; Schweingruber, 1990). Here, it is important to note that most studies described charcoal porosity as the total volume of nano pores (< 50nm). These nano pores are highlighted because of their contribution to high surface areas, which is considered to improve the adsorption of small dimensional molecules (Downie et al., 2009; Chan et al., 2009; Major et al., 2009). However, macro pores contribute to most of the pore volume of charcoal and are likely to play a role for the adsorption of large molecules (Keech et al., 2005) and the mobility of water, plant roots and microorganisms. The results of our study suggest that macro porosity is increased at high temperatures, which has also been reported for nano porosity (Macias-Garcia et al., 2004; Bornemann et al., 2007; Zabaniotou et al., 2008). Thus, high temperature charcoal could provide more volume and surface area.

The observed variation in pH was associated with temperature and residence time. Charcoal produced at high temperatures showed higher pH values than charcoal produced at low temperatures. This result corresponds to previous findings (Lehmann et. al, 2007a, Gundale

and De Luca, 2006). A potential explanation could be that basic inorganic ash material and their oxides accumulate with increased temperatures leading to an increase in the percentage ash content (Rutherford et al., 2008; Gundale and De Luca, 2006). Since the ash content of charcoal made from wood is generally low (Joseph et al., 2009), it was not possible to explain variation in charcoal pH by differences among species. In contrast, species effects have been found when comparing charcoal made from different plant materials (Tyron et al., 1948; Gaskin et al., 2008). Typically, charcoal pH is neutral to basic (Verheijen et al., 2010), which is consistent with our observed values. The effects charcoal pH might have on soil ecosystems have been under debate. Charcoal addition to soils has been shown to enhance soil pH (Rondon et al., 2007; Van Zwieten et al., 2007). However, De Luca and Gundale (2006) concluded that a pH increase of soil by charcoal application is unlikely and that it is more likely that charcoal creates local patches of alkalinity. Assuming that a wildfire has variable peak temperatures (Certini et al., 2005), it is likely that a variety of neutral to basic microsites are created. An increase in pH up to 7 is likely to favor the abundance of soil bacteria (Lehmann et al., 2011). Base cations are known to be protected against leaching at high pH and nitrate at moderate pH (Lehmann et al., 2002). In general, neutral pH values may promote nutrient (P and cation) availability (Warnock et al., 2007). Moreover, under alkaline conditions charcoal surfaces generally become negatively charged and increase the CEC (Amonette et al., 2009). Charcoal pH was also affected by the residence time and thus is not only dependent on fire intensity, but also on fire duration. The suggestion that charcoal can maintain a pH which differs from the surrounding soil is interesting and needs further field experimental evidence. Charcoal might then become a predictor of local soil conditions and processes, such as plant growth.

During charcoal formation organic nitrogen is converted to inorganic forms. Our results indicate that most NH_4^+ -N is lost at higher temperatures. N is an element that is considerably volatilized at temperatures $< 500^\circ\text{C}$ (Knicker et al., 2007). Additionally, it has been suggested that during the charring process NH_4^+ is oxidized to NO_3^- via nitrification (Certini et al., 2005; Gundale and De Luca, 2006). This might be a plausible explanation for the higher NO_3^- concentrations in high temperature charcoal. NH_4^+ might have a stimulatory effect on microbial abundance in low-fertile soils (Glaser et al., 2002; Gundale and De Luca, 2006; Lehmann et al., 2011). For available nutrient concentrations in charcoal we also observed significant time effects. Charcoal produced at a residence time of 45 minutes showed higher NH_4^+ concentrations than charcoal produced at shorter residence times. It is, however, unlikely that NH_4^+ would increase with time. Instead, NH_4^+ concentrations are likely to decrease over time. When the point of volatilization has been reached, only time is needed to reduce the concentration of ammonium. Temperature accelerates the process of NH_4^+ volatilization and diminishes the importance of time. Charcoal PO_4^{3-} concentrations were not significantly affected by species or fire conditions. However, *Pinus* charcoal tended to have somewhat lower PO_4^{3-} values than *Sorbus* charcoal. P has a higher thermal stability than N and its volatilization occurs preferentially between 700°C and 800°C (Gundale and De Luca, 2007). In contrast to De Luca and Gundale (2006), in our study the concentration of PO_4^{3-} was not significantly reduced at high temperatures. This discrepancy might be related to the different retention times used in both studies. De Luca and Gundale (2006) generated charcoal

that was heated for 2 hours and the naturally observed flame residence times of 5 -15 min used in our study might not be long enough to detect a significant difference. Nevertheless, both studies generally demonstrated increased nutrient retention capacities for PO_4^{3-} . Charcoal may thus constitute a potential long term reservoir of nutrients, which is protected against leaching and eventually available for plant growth.

Charcoal pore size distribution was only dependent on the type of wood, similar to what previously has also been observed by Keech et al. (2005). Keech et al. (2005) tested species responses at a fixed temperature of 450 °C. Here, we confirm their finding over a wide range of fire conditions. It has been shown that charcoal with a high proportion of macro pores (i.e. pore surfaces larger than 250 μm^2) has a higher adsorption capacity for allelopathic compounds, which in turn would reduce inhibitory effects on tree seedling growth in late successional forests of Northern Sweden (Keech et al., 2005). In this context, *Sorbus* — having a high density of macro pores — likely has a high adsorption capacity. A low surface tension may be the reason for macro pores to conduct water and soluble organic compounds easily in the charcoal matrix. Several studies have shown temperature effects on pore sizes distribution in the very far micro pore size region (Cetin et al., 2004; Zhang et al., 2004); however, in the macro region no significant effect of temperature has been reported (Downie et al., 2009).

It is likely that the observed pore size distribution plays a role for soil bacteria (average body size of 1 and 4 μm) and fungal hyphae (average body size of 1 to 64 μm) (Warnock et al., 2007)). *Betula* charcoal — having a large portion of micro pores (< 7 μm) — is likely to provide shelter for bacteria, whilst also having a large proportion of macro pores (> 18 μm) potentially utilized by a wide range of soil organisms. The same would be true for *Sorbus* charcoal, having a large proportion of macro pores. *Pinus* charcoal appeared to have a large proportion of meso pores. Interestingly, this meso pore region has the optimal diameter size to provide habitat for the largest portion of the fungal population (< 16 μm). Thus, each of the three charcoal types creates its own specific microhabitat, increasing the niche variability within soils and potentially promoting microbial diversity.

4.2. Experiment 2

The second experiment was done to compare the newly developed charring method (i.e, the barrel) with the more conventional and already established muffle furnace method (Wardle et al., 1998; Zackrisson et al., 1996; Keech et al., 2005; Pluchon in prep.). We did not observe any significant effects of charring method on charcoal traits. Using the barrel method, it also appeared that the temperature achieved in the gas flame was in agreement with the temperature generated in the muffle furnace. One of the drawbacks of with the isolated gas flame is the difficulty to run multiple samples at the same time keeping the temperature constant, which makes the method a bit more time consuming.

4.3. Experiment 3

It appeared that the electric conductivity is generally lower for charcoal produced from dead wood under wildfire conditions than for charcoal produced from the same wood in a barrel.

Further, we showed that charcoal produced under wildfire conditions had a significantly lower salt concentration than charcoal produced in a barrel. During both charring processes, the highest temperature was reached without a noticeable temperature gradient. Moreover, we observed the same flame residence times during both processes. In the wildfire, temperature fluctuations over the observed residence times were higher in comparison to the barrel. In the wildfire the short residence time at 900°C (one to two minutes) might have been ‘compensated for’ by the long exposure time at lower temperatures. As has been discussed before, charcoal pH and electric conductivity are both highly temperature dependent (see experiment 1) and it is mainly in these terms that we see a significant difference between the charring processes. This leaves the suggestion that high peak temperatures play a minor role in the formation of naturally produced charcoal. This could be the reason why we observed similar trait values for charcoal produced at lower temperature as for charcoal produced at 900 °C. The relative low pH of wildfire-produced charcoal corresponds to a relative low concentration of inorganic bases that were found in the wildfire charcoal. Surprisingly, higher concentrations of PO_4^{3-} were found in wildfire-produced charcoal than in barrel-produced charcoal. In our study, we used dead wood for charring under wildfire conditions. Partially decayed wood can be enriched in phosphorus (Prescott et al., 2002) and depleted in nitrogen due to fast microbial decomposition, nitrification or leaching processes (Boulanger and Sirois, 2006). Lower NH_4^+ -concentrations in the wildfire and the generally lower temperatures in the wildfire, may have restricted an increase in NO_3^- concentrations. The bulk density and transversal porosity of wildfire-produced charcoal was not significantly different from barrel-produced charcoal. The results of experiment 1 showed that there was no significant difference in transversal porosity between charcoal produced at 700 °C and at 900 °C. This might suggest that the wildfire charcoal was formed at around 700°C.

5. Conclusions

Experiment 1 provided evidence for the proposed interaction effects between species and fire conditions (i.e., temperature) on charcoal traits such as electric conductivity, density and transversal porosity. These findings provide new insights in how different tree species respond over a temperature gradient (450°C, 700°C and 900°C) in affecting charcoal traits. Observed interaction effects suggest that at a specific temperature the change in electric conductivity, density and transversal porosity is dependent on species. Importantly, from our study follows that chemical traits are more temperature dependent while physical /structural traits are more species dependent. Some previous studies have suggested that chemical charcoal properties might be species dependent (Glaser et al., 2002; Chan et al., 2009). However, in these studies the used species differed widely in their ash contents, which could explain differences in pH.

With our second experiment we could show that our new barrel method for charcoal production gives reliable and accurate results that are comparable with charcoal produced under laboratory conditions.

The results from our third experiment demonstrated that the physical properties (bulk density, pore size distribution, transversal porosity) of wildfire-produced *Pinus sylvestris* charcoal are comparable with charcoal produced from the same species under controlled conditions. This finding might have important implication for restoration of early successional forest in Northern Sweden. First, species (in this study *Pinus* and *Betula*) with a high amount of micro and meso pores can be used by microorganisms. Predator-prey relationships then become more predictable. Second, increased microbial abundance facilitates nutrient turnover in acidic phenol rich coniferous forests (Zackrisson et al., 1996). With the assumption in mind that charcoal containing higher amounts of macro pores exhibits also a high adsorption capacity towards phenolic substances (Keech et al., 2005), it is likely that forest stands composed of woody species with a large amount of macro pores (such as *Sorbus aucuparia*) might be suitable for fire restoration practices. In recent years, the use of fire as a restoration tool has slightly increased, due to increased awareness in forestry and politics of fire as a natural component of boreal forest ecosystems (Rydqvist and Kraus, 2010).

This study opens new possibilities for future experimental studies. Especially in Swedish boreal forest it should be tested whether the demonstrated species-dependent traits (bulk density, transversal porosity and pore size distribution) identified in natural charcoal, affect ecological processes and functions differently.

With the new awareness of interactions effects in the formation of charcoal, an important question evolved. What other chemical and physical traits show an interaction effect? This knowledge might improve our understanding of the high variability in charcoal and its specific role in the environment.

6. Acknowledgement

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8. Appendices

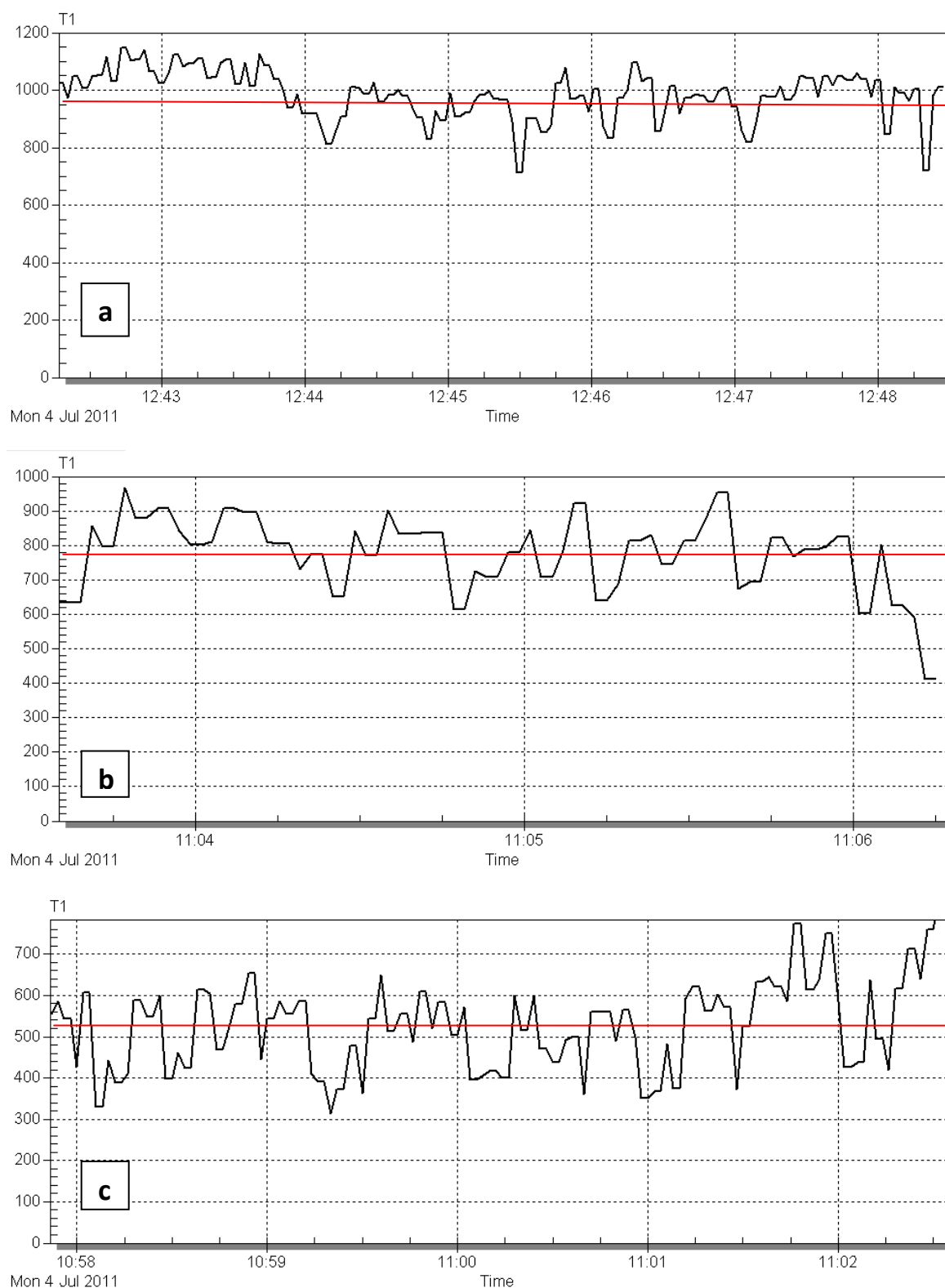


Figure S1: Thermocouple data of experiment 1 and 3 showing fluctuations of a gas flame used to generate charcoal at (a) 900°C, (b) 700°C and (c) 450°C. Temperature lines are fluctuating of $\pm 100^\circ\text{C}$ around the treatment temperature 900°C.

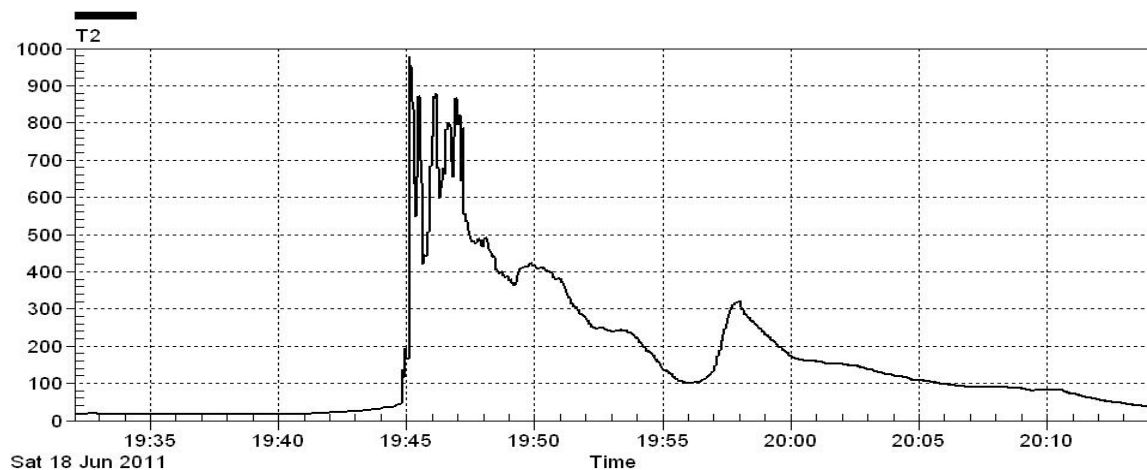


Figure S2: Thermocouple data illustrating the flame temperature at an observation point in a prescribed fire at Kärinsberget, Northern Sweden, during the formation of charcoal. The graph showcases how peak temperature (978°C) and flame residence time (about 15 min) were selected for the comparative analysis in experiment 3.

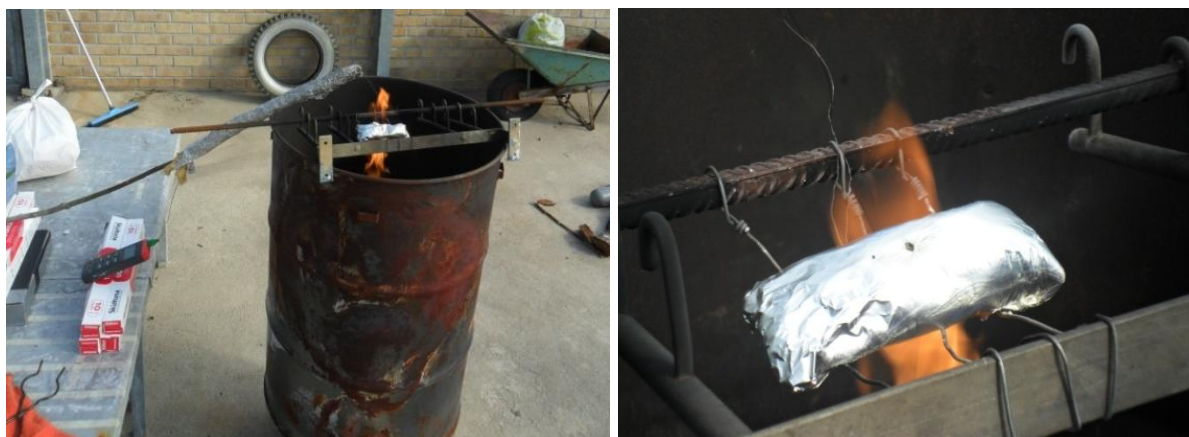


Figure S3: Barrel design used in exp 1 and 3. In order to test for the influence of species and fire conditions on the variability of charcoal traits, a range of temperatures (450°C , 700°C , 900°C), and residence times (5, 10 ,15 and 45 min), and a variety of species (*Betula*, *Pinus*, *Sorbus*) were chosen. Controlled conditions were established using a gas flame, a thermocouple reader and packages of wood simulating low oxygen conditions. As indicated in the picture at the right, volatilizing gases could escape from a small hole in the aluminum sheet.

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